Entropy and heat

0.0.1 Heat exchange between systems with infinitesimal temperature difference is reversible
If the system exchanges no work but only heat, and if the process is quasistatic, then

\[ dS = \frac{1}{T} dQ. \] (0.0.1)

Consider the situation in Fig. 0.0.1, where the system is initially at temperature \( T_0 \). Suppose the specific heat of the system (assuming it is a block of material) is \( C \).

![Figure 0.0.1: Heat contact with bath](image)

Then, \( dQ = C dT \). Therefore, the entropy increase of the system is, if we can realize a quasistatic process to ‘warm up’ the block,

\[ \delta S_{\text{sys}} = \int_{T_0}^{T_0 + \delta T} \frac{C}{T} dT = C \log \frac{T_0 + \delta T}{T_0} = C \log \left(1 + \frac{\delta T}{T_0}\right) = \frac{C \delta T}{T_0} - \frac{C}{2T_0^2} (\delta T)^2 + O[(\delta T)^3]. \] (0.0.2)

The entropy increase of the heat bath is, since it does not change its temperature,

\[ \delta S_{\text{bath}} = -\frac{C \delta T}{T_0 + \delta T} = -C \frac{\delta T}{T_0 (1 + \delta T/T_0)} = -C \frac{\delta T}{T_0} + \frac{C}{T_0^2} (\delta T)^2 + O[(\delta T)^3]. \] (0.0.3)

Therefore, the entropy change due to this heat contact is

\[ \delta S = \delta S_{\text{sys}} + \delta S_{\text{bath}} = \frac{C}{2T_0^2} (\delta T)^2 + O[(\delta T)^3]. \] (0.0.4)

It is indeed positive (irrespective of cooling or warming!) in harmony with the second law, but it is \( O[(\delta T)^2] \), so it is a higher order infinitesimal and does not add up to a finite amount. That is, the heat exchange between the systems with infinitesimal temperature difference is reversible.

0.0.2 Quasistatic temperature change due to heat
Exploiting the fact that the heat exchange between the systems with infinitesimal temperature difference is reversible 0.0.1, we can devise a means to change the temperature of any system in a quasistatic manner (i.e., reversibly). We prepare numerous heat baths with temperatures \( T_0 + \delta T, T_0 + 2\delta T, \ldots, T_1 - \delta T, T_1 \) and bring the system with initial temperature \( T_0 \) in contact with these heat baths successively to reach the final temperature \( T_1 \).
0.0.3 Exchanging (finite) heat with heat bath is always irreversible

However, generally heat transfer is irreversible. Consider the effect of a single heat bath of temperature $T_F$. Then system whose initial temperature is $T_0$ will reach temperature $T_1$ with the total entropy change given by

$$\Delta S = \int_{T_0}^{T_F} \frac{C}{T} dT - C \frac{T_F - T_0}{T_F} = C \log \frac{T_F}{T_0} - C \frac{T_F - T_0}{T_F} = C \left[ \log \frac{T_F}{T_0} + \frac{T_0}{T_F} - 1 \right]. \quad (0.0.5)$$

For $f(x) = \log x - 1/x + 1$, $f(1) = 0$ and $f'(x) = (x - 1)/x^2$, so $f$ is minimum at $x = 1$. Therefore, if $x \neq 1$, $f(x) > 0$. This means our $\Delta S > 0$ as long as $T_F \neq T_0$; irrespective of cooling or warming, heat conduction is irreversible.

0.0.4 Effects of intermediate temperature heat baths

Let us choose one more heat bath with temperature $T_1$ between $T_0$ and $T_F$. The total entropy change is given by

$$\Delta S = C \log \frac{T_1}{T_0} - C \frac{T_1 - T_0}{T_1} + C \log \frac{T_F}{T_1} - C \frac{T_F - T_1}{T_F}. \quad (0.0.6)$$

Assuming $T_F > T_0$, let us illustrate this case and the case with more intermediate heat baths (Fig. 0.0.2).

Figure 0.0.2: Left: One intermediate heat bath; Right: more numerous intermediate heat baths. The pale red shaded area is $\Delta S/C$.

In the figure the pale red shaded area is $\Delta S/C$, so increasing the intermediate heat baths filling the temperature gap reduces the ‘extent of irreversibility’ of heat conduction; the ultimate version was already discussed in 0.0.2; it is just the Riemann sum approximation of the integral.